

(12) **UK Patent Application** (19) **GB** (11) **2 135 696 A**

(43) Application published 5 Sep 1984

(21) Application No 8401458

(22) Date of filing 19 Jan 1984

(30) Priority data

(31) 58/005827 (32) 19 Jan 1983 (33) JP

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(51) INT CL³
C25B 9/00 1/46

(52) Domestic classification
C7B 145 234 273 278 279 283 503 510 511 512 525
526 551 552 554 AM

(56) Documents cited
GB 1587897 US 4279731
GB 1581348 JP 78/43377
GB 1503799

(58) Field of search
C7B

(54) **Electrolytic cell**

(57) An electrolytic cell of single electrode or multiple electrodes type, which is divided into an anode chamber and a cathode chamber by a cation exchange membrane (14) comprises a partition (2) (8) having a thickness of less than 6 mm separating the anode chamber from the cathode chamber, and ribs (3) joining the electrode (4) with the partition (2).

The cell is used for the electrolysis of an aqueous solution of an alkali metal chloride.

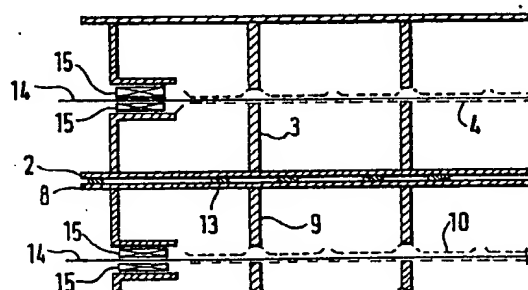


FIG. 4.

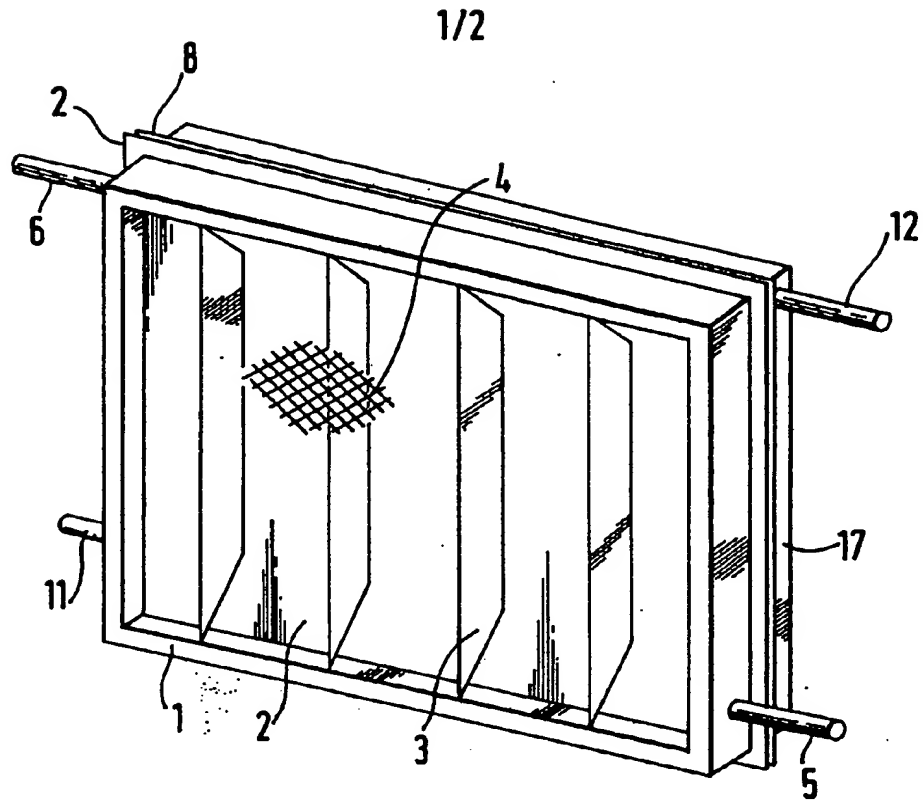


FIG. 1.

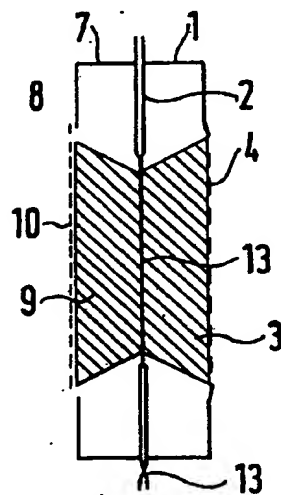


FIG. 2.

SPECIFICATION Electrolytic Cell

The present invention relates to an electrolytic cell for the electrolysis of an aqueous solution of alkali chloride.

A process is known for producing chlorine and caustic soda by means of the electrolysis of a common salt solution employing a cation exchange membrane as a diaphragm. The electrolytic employing the cation exchange membrane is a process which has recently attracted attention since the amount of common salt contaminating the caustic soda solution produced at cathode is extremely low and since there are no pollution problems as compared with the known mercury method, the asbestos diaphragm method or the like.

As a result of the development and the improvement of the cation exchange membrane in order to raise the concentration of the caustic soda solution produced in the cathode chamber and also the efficiency of the current, it has become possible recently to obtain a caustic soda solution having a concentration of over 30% with a high current efficiency of more than 90%. Moreover, a cation exchange membrane based on the perfluorocarbon polymer has been developed and has now been commercialized to some extent.

On the other hand, the importance of energy conservation has recently been recognized throughout the world and it is strongly desired that the electrolytic power, that is the electrolytic voltage of the electrolytic cell, to be decreased to as low as a value as possible.

In the past, various means were proposed to remove the generated gas more easily to the rear side of the electrode for the purpose of lowering the voltage of the electrolytic cell.

There are known processes employing porous electrodes such as expanded metal, punched metal, metallic wire etc., and specifying the composition or the type of exchange group of the cation exchange membrane, and the like.

Moreover, as the means for lowering in the voltage of the electrolytic cell, such modifications of the structure of the cell as the circulation of liquid, the separation of gas from liquid, the reduction of distance between electrodes, and the like have been proposed. Furthermore, recently, an electrolyzing process where the distance between the electrodes is substantially zero and the electrodes closely contact the membrane, called the SPE process (Solid Polymer Electrolyte Process), is laid open under, for example, Japan Unexamined Patent Publication No. 102278/1978 with a view to saving energy.

Also, for the purpose of a further reduction in the power consumption, similarly from a standpoint of saving energy, various developments of the cathode having a hydrogen overvoltage lower than iron have been made, as laid open publicly, for example, under Japan

Unexamined Patent Publication No. 92295/1980, No. 61248/1981.

However, in these processes employing an active cathode, a phenomenon is observed in that the concentration of iron ions in the caustic soda solution in the cathode chamber increases dramatically for a short period. This phenomenon is further apparent to an even higher extent under the severe electrolytic conditions needed to provide a higher temperature and a higher alkali concentration. Therefore, it is conceivable that the cathode chamber should be constructed using nickel metal having a corrosion resistance to alkali.

However, it is considered that the use of nickel material for all the construction metal of the cathode chamber as a substitute for carbon steel is expensive and impractical. With regard to the electrolytic cell employing the cation exchange membrane, both a double electrode type and a single electrode type in filter press form are used presently as practical cells.

However, owing to the structure of the electrolytic cell, the feeding-discharging system of current is complicated in the case of the latter type, whereas the electrically connecting system in the partition between the cathode chamber and the anode chamber is apt to become complicated in the case of the former type.

As an electrically connecting system used in the double electrode type, a screwing-in type or an explosively welding type inserting a metal having a resistance to the hydrogen permeability is laid open under, for example, Japan Unexamined Patent Publication No. 43377/1976. This has, however, many difficulties such as an increase in the resistance when running of the electrolytic cell over a long period a rapid occurrence of corrosion, and high costs.

The present invention provides an electrolytic cell for the electrolysis of aqueous solution of alkali halide, which is divided into an anode chamber and a cathode chamber and employs a cation exchange membrane, wherein a partition having a thickness of less than 6 mm separates the anode chamber from the cathode chamber and ribs join the electrode with the partition.

Either a double electrode type or a single electrode type may be used as an electrolytic cell.

As to the partition separating the anode chamber from the cathode chamber, the partition in the side of the anode chamber and that in the side of the cathode chamber may be joined under compression by using the continuous seam weld method. Also, a reduction in the weight of the electrolytic cell is provided by decreasing the thickness of the partition material. Furthermore, a reduction in the voltage of the electrolytic cell is achieved by narrowing the distance between the partition and the electrode and setting the gap between the anode and the cathode facing to each other across the cation exchange membrane to be as near to the thickness of the membrane as possible.

Thus, a result of extensive investigations in

order to solve the problems of the prior art, the inventors have found that, in an electrolytic cell for alkali halide employing a cation exchange membrane as a diaphragm, a high concentration of the caustic soda solution can be obtained with a high current efficiency by making the thickness of the partition as thin as possible, reducing the weight of the electrolytic cell, narrowing the distance between the partition and the electrode, and so on, without using the screwing-in method or the explosively welding method for the joining of the metallic partition material having a corrosion resistance in the cathode chamber with that in the anode chamber.

In following, an exemplary embodiment of a double electrode type electrolytic cell of the invention will be illustrated, with reference to the accompanying drawings, wherein:

Fig. 1 is a view showing the construction of the double electrode type electrolytic cell;

Figs. 2 and 3 show a vertical and a horizontal cross-sections of the electrode chamber of the invention, respectively; and

Fig. 4 is a horizontal cross-section showing the assembled state the cation exchange membrane, the cathode and the cathode chamber material, the anode and the anode chamber material, and the gasket etc.

Fig. 1 shows a frame 1 for the anode chamber in the form of a picture frame to fix the thin plate partition 2 in the anode chamber. Rib 3 conducts the electricity from the partition 2 to the anode. 4 is the anode. 5 is a feed nozzle for the saline water. 6 is an ejection nozzle for chlorine gas generated on electrolysis and the solution in the anode chamber. Materials used for 1 to 6 are all based on Ti or Ti alloy having a corrosion resistance to chlorine. 7 is a frame for the cathode chamber in the form of a picture frame to fix the partition. 11 is a feed nozzle for the pure water or the alkali metal solution. 12 is an ejection nozzle for hydrogen gas generated on electrolysis. Materials used for 7 to 12 are all based on a metal having a corrosion resistance to alkali metal, for example, nickel or stainless steel. In Fig. 2, 8 is a thin plate partition in the cathode chamber. 9 is a rib to conduct the electricity from the cathode to the partition. 10 is the cathode. 13 is the partition joined by a wavy continuous seam weld.

When electrolysis is carried out by feeding the saline water or the pure water (or the dilute alkali metal solution) to the fixed portion of the double electrode type electrolytic cell shown in Fig. 1, the current passed through the ion exchange membrane flows from the cathode to the ribs in the cathode chamber to the partition in the cathode chamber to the seam welded portion to the partition in the anode chamber to the ribs in the anode chamber to the anode and to the next ion exchange membrane.

At the anode, the anode reaction takes place resulting in the generation of chlorine gas. As said electrode is constructed substantially close to the cation exchange membrane, gas generated by the

electrolysis is ejected rapidly behind the electrode without remaining in the space between the membrane and the electrode, and is ejected outside of the electrolytic cell together with the anode solution through the ejection nozzle located at an upper part of the electrode chamber. At the cathode, hydrogen gas and alkali metal solution are formed by the cathode reaction. The formed products are ejected through the ejection nozzle located at an upper part in almost same flowing state as in the anode chamber.

Next, the relationship of each element used for the electrolytic cell of the invention will be explained in detail.

The cation exchange membrane is a membrane generally used, the functional group thereof being carboxylic acid group, sulfonic acid group, mixed acid group thereof, or the like, and may be either a hydrocarbon-based cation exchange membrane or a perfluorocarbon-based one. Further, both surfaces of the membrane may be plain and smooth, but preferably one or both of the surfaces is roughened or has fine porous layers. As the anode, it is recommended that, for example, conventional platinum group metals, their alloys or the oxides of platinum group metals are used through coating or sintering onto the conventional titanium substrate. As the cathode, it is desirable that platinum group metals, nickel, cobalt, chromium or the alloy metals thereof are used, or the metals having a low hydrogen overvoltage are used through metal plating or melt spraying onto the iron-based metal substrate.

The form of the electrodes in both electrode chambers should be porous bodies such as expanded metal, punched metal, wire mesh etc. maintaining gas permeability and liquid permeability. Moreover, the surface of the electrode contacting the ion exchange membrane is to be completely connected to the ribs both electrically and mechanically as well as to being made plain and smooth by machining etc. The size of the electrodes is preferably fine in order to make the electrode in at least one electrode chamber flexible, and as a preferred example, it can be said that the opening ratio is 30 to 70%, the thickness is 0.1 to 1 mm and the width, that is the shortest distance from the circumference of one open portion to the nearest adjacent open portion, is less than 5 mm. Further, in order to make the whole electrode flexible, the electrode joined with ribs connecting the electrode to the partition is divided wholly or partially in the neighbourhood of the centre between one rib and the other rib, as shown by 10 in Fig. 3. Also, if an angle formed by the surface of the electrode extended from the rib to both sides against the surface of the membrane is equal to or less than 180°, as can be seen from Fig. 4, the surface of the electrode cannot be pressed against said membrane so strongly even if a part of it contacts the membrane, so that a constant function can be maintained without any mechanical damage to the membrane, when operating by setting the gap between the anode joined with the anode ribs and

the cathode joined with the cathode ribs to approach to thickness of the cation exchange membrane as nearly as possible through said membrane. And yet, the dimensions and the shape of the said fine electrode are not limited to the cathode shown in the figures.

The width of the frame for the electrode chamber is determined by the distance from the surface of the electrode facing the ion exchange membrane to the surface of the partition contacting the electrolytic solution in either anode chamber or cathode chamber. Although the said distance is preferably as narrow as possible to decrease the voltage drop due to the electric resistance of ribs connecting the electrode to the partition electrically, preferably said distance is from 10 to 25 mm due to the requirement to allow gas generated by the electrolysis to escape easily from the electrolytic solution. With regard to the material of the frame for the electrode chambers, the frame for the anode should preferably be made of titanium or titanium containing a minor amount of palladium, and that for the cathode should preferably be made of nickel, stainless steel or iron-based metals.

Fig. 2 is a vertical cross-section of the double electrode type electrolytic cell when the thin plate partition and the fine electrode of the invention are installed as the cathode. In the figure 4 is the anode, 3 is an anode rib to feed the electricity to the anode, 10 is the cathode, and 9 is a cathode rib to conduct the electricity from the cathode to the partition. The respective electrode in each electrode chamber and the ribs are preferably joined both mechanically and electrically by welding. In Fig. 2, is the partition in the anode chamber and 8 is that in the cathode chamber. 13 is the partition joined by a wavy continuous seam weld. As materials for the partition, titanium is desirable for the anode side and nickel or stainless steel is desirable for the cathode side. The thickness of the partition is substantially the sum of the thickness of the partition on the anode side and that on the cathode side. Although the partition is preferably as thick as possible in order to realize a better planar property, its thickness should be less than 6 mm according to the characteristic of the invention aiming at reducing the weight of the electrolytic cell. It is not necessary to provide the wavy continuous seam weld on the whole surface of the partition. Welding is sufficient if provided at least by a length equivalent to that of the rib in the neighbourhood of the anode rib or the cathode rib. The area of the portion of the wavy continuous seam weld is 1/500 to 1/10 of the effective current area of the cation exchange membrane, preferably 1/100 to 1/20.

Fig. 3 is a horizontal cross-section of the double electrode type electrolytic cell when the thin plate partition and the fine electrode are installed as the cathode. 10 is the fine electrode. In order to exhibit more flexibility, the surface of the electrode joined there with the ribs is preferably set nearer to the partition than the

surface of the cathode formed when operating by setting the gap between the anode joined with the anode ribs and the cathode joined with the cathode ribs to approach the thickness of the cation exchange membrane as nearly as possible through said membrane, as shown in Fig. 4. The distance from the surface of the electrode joined there with the ribs to the surface of the cathode on running is desirably more than 2 mm and less than ten times of the thickness of the electrode.

For a clearer understanding, a horizontal cross-section of the double electrode type electrolytic cell assembled with all the constitutional elements is shown in Fig. 4. In Fig. 4, 15 is a gasket made of chloroprene rubber, EPDM or fluoro rubber which dissolves out less heavy metals such as calcium, magnesium, Pb, etc. 4 is the anode and 10 is the cathode. The numbers attached to the other parts correspond to those described above.

However, the shape, the dimensions or the form of the cathode 10 is not limited to the cathode shown in the figure. In following, applications of the electrolytic cell of the invention are described as examples.

EXAMPLE 1

A titanium plate with a length of one side of 1200 mm, that of the other side of 1200 mm and a thickness of 1.5 mm was joined under compression by a wavy continuous seam weld with a nickel plate with a length of one side of 1200 mm, that of the other side of 1200 mm and a thickness of 2.0 mm to obtain a partition separating the anode chamber from the cathode chamber. The width of the frames for the electrode chambers was 15 mm in the side of the anode chamber and 20 mm in the side of the cathode chamber. Eight anode ribs made of titanium plate with a thickness of 2 mm were provided on the anode side of the partition at intervals of 150 mm. Similarly, cathode ribs made of nickel plate with a thickness of 2 mm were provided on the cathode side of the partition at the same intervals as those of the anode ribs.

As the anode, a porous electrode was used which was obtained by the $\frac{1}{2}$ roll processing of the expand metal with $\frac{1}{2}$ inch activated through baking for 4 hours at 360°C after coating ruthenium chloride on the whole surface of the titanium substrate. As the cathode, M-60 micro mesh (made by Katsurada Grating Co.) was cut to a width of 150 mm and a length of 1200 mm and joined at the centre of the width of 150 mm in the longitudinal direction with the cathode ribs by spot welding, bending to the side of the surface of the membrane so as to form an angle by the surface of the electrode extended from the joint with the rib to both sides of 170°.

As the cation exchange membrane, a copolymer was obtained from monomers $\text{CF}_2=\text{CF}_2$ and



by copolymerizing in 1,1,2-trichloro-1,2,2-trifluoroethane using perfluoropropionylperoxide as an initiator (exchange capacity is 0.91 meq/g as sulfonic acid group) (A polymer). Similarly, a
5 copolymer was obtained from $\text{CF}_2=\text{CF}_2$ and



(exchange capacity is 1.1 meq/g as carboxylic acid group) (B polymer).

After A polymer and B polymer were moulded
10 into films having a thickness of 4 mil (0.1 mm) and 3 mil (0.075 mm), respectively, these two films were heat-pressed to obtain a sheet of film. Then the film was hydrolyzed for 6 hours at 80°C with NaOH/methanol (weight ratio 1/1) of a
15 concentration of 10 wt. % to obtain a cation exchange membrane.

Then the membrane, the cathode and the anode obtained as described above were joined with the frame of electrolysis, gaskets with a
20 thickness of 2 mm were adhered to the frames for both the anode and the cathode, and a multicell filter press type electrolytic cell was made assembling by turns so the electrodes contact to the membrane closely. Finally, after providing end
25 plates to both ends and tightening up uniformly with a tie rod, a double electrode type electrolytic cell was completed.

The direct current source was connected to each bus bar on both ends of the electrolytic cell.
30 Then, the electrolysis of the saline water was carried out under following conditions.

	Concentration of the feed saline water	200 g/l
35	Concentration of the produced caustic soda	35 wt. %
	Current density	30 A/dm ² (3000 A/mm ²)
	Temperature of electrolytic cell	90°C
40	Voltage per electrolytic cell	3.20 V

EXAMPLE 2

Using M-60 micro mesh electrode as the cathode which was activated by nickel metal plating employing the nickel both containing Ni
45 salt, thiourea solution of a concentration of 0.01 to 1.0 mol and/or at least one of the salts of oxo acids having an oxidation number of sulfur of less than 5, and ammonium ion having a concentration of more than 10.5 times mol to the

50 concentration of sulfur, the electrolysis was carried out under the same running conditions as Example 1. The voltage of the electrolytic cell thereby was 3.00 V. Furthermore, the inactivation of the activated cathode was never recognized
55 even on the running for 200 days.

CLAIMS

1. An electrolytic cell for the electrolysis of aqueous solution of alkali halide which is divided into an anode chamber and a cathode chamber
60 and employs a cation exchange membrane, wherein a partition having a thickness of less than 6 mm separates the anode chamber from the cathode chamber, and ribs join the electrode with the partition.

65 2. An electrolytic cell as claimed in claim 1, wherein the partition separating the anode chamber from the cathode chamber comprises a partition in the side of the anode chamber and one in the side of the cathode chamber joined by a wavy continuous seam weld.

70 3. An electrolytic cell as claimed in claim 1 or 2, wherein a distance from the surface of the electrode facing the cation exchange membrane to the surface of the partition contacting the electrolytic solution is within a range of 10 to 25
75 mm in either anode chamber or cathode chamber.

4. An electrolytic cell as described in any preceding claim, wherein the anode and the cathode comprise porous electrodes having an
80 opening ratio of 30 to 70% and a thickness of 0.1 to 1 mm, and wherein the distance from the circumference of one opening to that of the nearest adjacent opening is less than 5 mm.

5. An electrolytic cell as claimed in any
85 preceding claim, the electrode thereof being a porous electrode joined with ribs connected to the partition electrically and partly divided in the neighbourhood of the centre between one rib and the other rib, an angle being formed by the
90 surface of the electrode extended from the rib to both sides against the surface of the membrane of less than 180°.

6. An electrolytic cell as claimed in any preceding claim, the anode being joined with
95 anode ribs and the cathode joined with cathode ribs thereof being set through the cation exchange membrane to approach the thickness of said membrane as nearly as possible.

7. An electrolytic cell as claimed in any
100 preceding claim, wherein the material of the anode is titanium and that of the cathode is nickel or stainless steel.

8. An electrolytic cell substantially as herein described with reference to the accompanying
105 drawings.